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13. ABSTRACT (Maximum 200 words)

Our research under the contract is to investigate crystalline laser host materials and not the glasses. However, even with crystalline laser host materials where the thermal conductivity is much higher, it is still necessary to use slab geometry for high power operations with high repetition. Given the same geometry, material that has high thermal conductivity and high thermal mechanical strength is definitely preferred. Under this contract, we conducted a serious research on high thermal conducting laser host materials. We find the limitation on how far we can push the material. Unfortunately, it is in total conflict between the need of high thermal conductivity and the capability to host large active lazing elements. Materials with high thermal conductivity are in general very simple structure with low coordination and low atomic number elements with covalent bonding. Good examples high thermal conducting materials include diamond, silicon, SiC, BeO, GaAs, etc. We normally consider sapphire (AI203) the best thermal conducting solid state laser host material for Cr32+ and Ti3+. In reality, it is only a mediocre thermal conductor. In recent work of GaN on sapphire, the poor thermal conductivity of sapphire was sited as the major problem for the performance of high brightness blue LEDs and LDs.

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Introduction:

Solid state laser has discovered near four decades. Tremendous progress has been achieved during this period. The size of solid state laser can vary from smaller than a thumb nail (the microchip laser) to greater than a foot ball field (the NIF laser). The output power also varies by more than 10 order of magnitude. The overall efficiency is continuously improving due to the improvement of both the laser host material and the laser engineering.

The introduction of diode pumping has greatly improved the laser performance due to the reduction of thermal loading. The laser is miniaturized without sacrificing the output power. All of a sudden, we are able to use laser host which will not survive under lamp pumping condition but will perform well with diode pumping. This provides the incentive to search for new material aiming to improve the performance for special purpose, such as lasing at a specific wavelength. Part of our research effort is geared to this purpose.

On the other hand, there is also a general demand for high average power solid state lasers for both military and industrial applications. The traditional active lasing element is Nd. However, with diode pumping, there is real advantage to look Yb as the active lasing element. While the lasing transitions in Nd hosts are more predictable, it is not quite the case for Yb hosts. Moreover, a good host for Nd laser does not necessarily be a good host for Yb. For example, some of the best laser hosts for Nd include YAG, FAP and YVO_4. It is quite normal to expect that they all also are good Yb laser host. Our investigation under this contract shows that it is not quite the case. For diode pumped miniature Nd laser, the best host is YVO_4 followed by FAP with YAG the worst among the three. For diode pumped miniature Yb laser, the best host is FAP followed by YAG with YVO_4 the worst among the three. In fact, the spectroscopic overlapping between the absorption and emission spectra of Yb:YVO_4 is so bad that it can not be lased at all. The result shows that we can not always rely on simple instinct or common sense to make prediction of lasing behavior of a particular active ion in a particular host

material. This unpredictability poses greater challenge in the search of new Yb laser hosts. Our knowledge on optical materials is the great strength to carry out this contract.

For very high power applications where the laser output is greater than 100 watts up to a few kilowatts in the industrial cutting and welding condition, the criteria of a laser host is totally different. Since so much heat is generated during the lasing operation, the laser rod is frequently stressed to reach its thermal-mechanical limit. In this case, the spectroscopic behavior of the active lasing element is no longer the primary issue for the selection of a laser, but rather the thermal conductivity and the thermal mechanical strength of the host materials. With the existing material of finite thermal mechanical strength, the best approach to overcome the thermal issue is to use the slab geometry so that one of the lasing host dimensions is small to enhance the heat removal. The classic example of such a slab laser is the NOVA laser at Lawrence Livermore National Laboratory. Its lasing host is Nd doped phosphate glass which does not have very good thermal conductivity at all. Even with the slab geometry, it is still a single shot laser and can not achieve the high repetition rate. The new and still under construction NIF laser is also based on the same design.

Our research under the contract is to investigate crystalline laser host materials and not the glasses. However, even with crystalline laser host materials where the thermal conductivity is much higher, it is still necessary to use slab geometry for high power operations with high repetition. Given the same geometry, material that has high thermal conductivity and high thermal mechanical strength is definitely preferred.

Under this contract, we conducted a serious research on high thermal conducting laser host materials. We find the limitation on how far we can push the material. Unfortunately, it is in total conflict between the need of high thermal conductivity and the capability to host large active lasing elements. Materials with high thermal conductivity are in general very simple structure with low coordination and low atomic number elements with covalent bonding. Good examples high thermal conducting materials include diamond, silicon, SiC, BeO, GaAs, etc. We normally consider sapphire (Al_2O_3) as the best thermal conducting solid state laser host material for Cr^{3}_{+} and Ti^{3+}. In reality, it is only a mediocre thermal conductor. In recent work of GaN on sapphire, the poor thermal conductivity of sapphire was sited as the major problem for the performance of high brightness blue LEDs and LDs.

To be able to host large diameter active lasing elements such as Nd and Yb, you will need the host crystal containing large ion site. For most crystal structure, this means an increase of structural complexity and coordination, and thus rapid reduction of thermal conductivity. We have investigated a number of crystals and it comes out with this consistent pattern. The reason sapphire is not as good a thermal conductor as BeO is because it contains 6-fold coordinates rather than 4-fold ones. For rare earth containing crystals so far the best one is still YAG ($Y_3Al_5O_{12}$) which contains 8-fold coordinated Y site and 6- and 4-fold coordinated Al site. Even though the crystal has a few drawbacks such as the cubic symmetry, it is still by far the best material. The reasons are: (1) well established material and readily available, (2) capable to grow very large high quality crystals. (3) Isoelectronic substitution without charge compensation, (4) physically strong

without cleavage, and (5) tolerable thermal conductivity. Given all these good properties, the actual lasing performance is not on the top priority. In fact, there are many crystals that have better spectroscopic properties than Nd:YAG but simply can not deliver the kind of power needed for most applications. To be able to deliver even higher power would require larger slab configuration so that it is possible to manage the thermal dissipation problem. One of the tasks of our research is aimed to resolve this issue.

In addition to tackle the thermal problem of Nd:YAG, we are also look into the more fundamental issue, i.e., the improve the thermal loading issue. On this respect, one way to reduce the thermal load is to have smaller quantum defect. The reason to search for Yb laser is because of its small quantum defects and simple radiative transitions. The best known Yb laser includes Yb:YAG, Yb:SFAP, etc. The thermal loading in these Yb laser is much less than that in Nd laser. Therefore for the same laser host material, Yb laser can deliver more power only if the Yb transitions behave. Unfortunately, we have indicated before that there is no good rule to follow to look for a good Yb laser host. The only way to find out is to actually dope the crystal with Yb and then measure its spectroscopic properties.

Another way to reduce thermal loading is to search for host crystals with high thermal conductivity. I have mentioned the rules earlier. Using the rules, the best thermal conducting rare earth containing laser hosts are yttria (Y_2O_3), lutecia (Lu_2O_3) and scandia (Sc_2O_3). Unfortunately, all three materials are highly refractory with melting temperature above 2400°C. So far people are only able to make small pieces of

these crystals by arc lamp zone melting, flux growth and Bridgman gradient freeze. Yttria has a solid state phase transition and thus can not be grown directly from the melt. Both lutecia and scandia appear to melt congruently and also without solid state phase transition. However. no one is able to grow these crystals by pulling from the melt. In my laboratory, we do not have any facility capable to melt these materials because of the extremely high melting temperatures. However, these materials do represent a new hope to achieve high average power solid state laser only if we can produce high quality single crystals.

In addition to the active solid state laser hosts, there is also interest to look for non-linear optical crystals which are capable to handle high power harmonic conversions. Traditional non-linear optical materials such as KTP, BBO and LBO are not congruent melting so that they have to be grown from flux. As a result, the growth rate is very slow and the crystal size is also small. This limits the size of aperture which can handle the laser beams. Luckily, in recent years, there are reports on the discovery of CLBO and GdCOB and YCOB single crystals. All of them are congruent melting and capable to produce very large single crystals. We have done extensive investigation on all three materials and discovery interesting results which turns out to be critical for the utilizing of these crystal in practical applications.

Search for New Laser Host Materials:

One of the primary objectives of this investigation is to look for new solid state lasers. The search criteria is that all these new lasers are diode pumpable. This means that the absorption of the active ion must have a spectrum match to the emission of the pumped diodes. This is not so hard for Nd or Yb doped solid state lasers since there are plenty high power diodes or diode bars in the 800 to 980 nm region.

For UV lasers based on Ce doping, there is no suitable diode pump source. The most likely pump source will be diode pumped Q-switched 4^{th} harmonic Nd:YAG lasers at 266 nm. Despite of lack of cheap pump source, tunable UV laser source is interesting and very useful as chemical sensors. We have developed Ce-doped LiSAF and LiCAF before as good tunable UV laser. We also investigated a new laser host, $SrAlF_5$, doped with Ce. High quality single crystal has been produced. We have done the absorption, emission and fluorescence lifetime measurements. The result shows that Ce-doped $SrAlF_5$ is indeed a promising laser hosts. Ce-doped fluorides provide the only tunable UV solid state laser source to date. Even though it has many potential applications, the main drawback is the lack of low cost pump source. The overall cost of the entire laser system has become prohibitive high. It will find its niche application in the Research Institutions and not that much commercial ones.

In the near IR region, we have been seeking alternative laser host which might replace Nd:YAG for high power applications. We approach the problem in two directions: higher thermal mechanical strength material and lower thermal loading (or quantum defect) material.

(A) High thermal mechanical strength material:

We are seeking materials that is hard without cleavage planes and has high thermal conductivity. In other word, the crystal is robust. Materials that fit to this description typically consist of light elements with low coordination covalent bonds. Unfortunately, this is just the opposite for the doping requirement of large rare earth elements such as Nd. All the rare earth elements are quite heavy and very large in ionic size. The most comfort coordination is 8 or higher. Even 6-fold coordination site is considered very tight. Only very few 6-fold structure compounds are capable to accommodate very small amount of rare earth elements into the structure. The ones that can get in are inevitably the smaller size rare earth elements such as Er, Ho, Tm, Yb and definitely not Nd. I have looked into a number of crystals with most of the content of small and light elements and only one large site for the doping of the active ion. Unfortunately, the moment there is a high coordination site, the thermal conductivity drops quickly below that of YAG making the crystal useless for the purpose.

Nevertheless, there is one class of oxide material which has very high thermal conductivity. They are rare earth oxide with the general formula of R_2O_3 where R = Y, Lu and Sc. They are simple oxides with coordination of 6 only. This type of material is highly refractory with melting temperature exceeding 2400°C. At present time, it is actively studied at University of Hamburg. Because of the high melting temperature, small crystals have been produced by arc lamp melting and by flux growth. In our

laboratory, we only have Iridium crucible which has a melting temperature of 2460°C and thus not suitable to grow these crystals. Researchers at University of Hamburg use rhenium crucible to melt these charges. But rhenium is not an easy metal to work with since it is sensitive to oxygen. It requires the use of vacuum sealed furnace. So far, no one is able to pull single crystal from melt. The standard procedure is just to melt and freeze the charge slowly to get large grains of the crystal. Single crystal pieces were then cored out from the crucible for investigation. Among the three compositions, Y_2O_3 has the largest cation and thus the best chance to incorporate large rare earth ions but simply because of the larger ionic size it has a solid state phase transition and thus not useful. Sc_2O_3 has the smallest cation size and thus the most stable compound among the three. At the same time, it has the least solubility of large rare earth ions in its structure. Again, we are fighting a losing war in the sense that there simply does not exist any material which can have both high thermal conductivity and high large rare earth ion doping at the same time. The best chance for a reasonable laser would be Lu_2O_3 heavily doped with Yb. Another point to make is that so far there is no easy way to grow large high quality crystals of these compositions because of the extremely high melting temperature. This could be the ultimate limitation to use these crystals in practical applications.

(B) Low thermal loading (or quantum defect) material:

The second approach to high average power solid state lasers is to reduce thermal

loading so that the material will not be fractured by the excessive heat. Thermal loading normally comes from two sources: absorption of pumped lamp power and heat release due to quantum defect. The first one is due to the absorption of the broad band emission spectra of the flash lamp. Energy is absorbed by both the host crystal absorption bands and all the transitions of the active ions. But not all the energy absorbed by the active ions is released by radiative emission. In fact, the majority is emitted non-radiatively as heat. The second one comes from the energy difference of the excitation and emission bands of the lasing transition. This difference will again come out as heat. Thermal loading can easily fracture a crystal if it has poor thermal conductivity and is not properly cooled.

We have mentioned that it is highly unlikely that we can found good laser host that can accept the large rare earth active ions and also has high thermal conductivity. The other way to minimize the thermal problem is to reduce the heat production during lasing action. Diode pumping is one ideal way to reduce thermal loading since the pump energy is fully matches to the absorption band of the active ion and there is no waste. However, even under diode pumping condition, the quantum defect will still produce the heat that equals to the energy difference between the excited state and the terminal state. This amount of heat can also be significant if the total energy of extraction of lasing action is not high. Among all the rare earth ions, Yb^{3+} has the simplest transition structure and no excited state absorption. The quantum defect is also quite small as compared to that of Nd^{3+} ion because of the smaller Stock shift. Historically, it is an ion that everyone likes but no one has a good means to pump it effectively because it only

has very narrow absorption bands in the near IR region. Diode pumping resolves this problem nicely. The long fluorescence lifetime is also a nice feature so that less diode is needed for the pump. Finally, pumping in the 900 nm region would allow the use of InGaAs laser diodes which is far more robust as compared to AlGaAs laser diodes.

Given all these nice features, we have investigated extensively, in this research, on the Yb laser hosts. We have investigated Yb-FAP, Yb-SFAP and Yb-SVAP in the apatite structure compounds. Spectroscopically, these Yb-doped apatite structure compounds have the best property than any other known Yb-doped materials. We have published more than one dozen papers on this subject. We have demonstrated excellent lasing action in these host crystals. Unfortunately, they also have serious drawbacks. The three fundamental problems of these apatite structure compounds are:

(1) They have the growth defects due to the unique "parting" or slip plane property of the crystal. It causes optical non-uniformity of the crystal over a large cross-section area or along a long optical path. We have tried many different approaches to eliminating the problem with limited success. One possible way to reduce such effect is to grow off-axis crystals such that the growth direction is at an oblique angle to any of the crystallographic axes. The draw back of this approach is the limited length of the laser rods that can be harvested. It is also very difficult to fabricate the crystal with very large material waste.

(2) The crystal can easily form opaque white cloudy region at the center of the crystal. Annealing can eliminate the cloudiness but the opaque white material seems to accumulated to form long stringer of inclusions at the core region of the crystal. This may caused by the non-stoichiometric composition of the crystal which tends to expel the excess ingredient. So far we were unable to identify the nature of the inclusion. Some incomplete micro-analysis tests tend to indicate that they are actually rare earth oxide (or the dopant).

(3) Since the rare earth dopants are 3+ charged and the substituted alkali-earth elements (Ca, or Sr) are 2+ charged, there is charge compensation issue for the incorporation of the dopants within the structure. The most accepted model is the pair substitution of $Sr^{2+} + F^-$ by $Yb^{3+} + O^{2-}$. Unfortunately, we found that the total amount of substitution is quite limited. Higher doping will make the crystal milky and useless. This is the most serious limitation for the use apatite structure compounds as Yb laser host.

To summarize, despite the superior spectroscopic and lasing properies of the apatite structure compounds, the limitation of them is due to the fact that it is not possible to grow high quality large size single crystals with high doping. This limitation is not due to the growth technology but the intrinsic structure property of the crystals. It is somewhat disappointing after all the efforts that have put on over the years.

Because of the problem to produce large size Yb-doped FAP, SFAP, SVAP single crystals, we also start to look into other possible structure compounds as Yb laser host. Unfortunately, there is no clear methodology for such a search process. One common starting point is to look for a good Nd laser host and then doped it with Yb. It turns out that this approach has no basis at all. Even though both Nd:YAG and Yb:YAG are good lasers, it is just a pure coincidence and does not apply to other crystal structures. I have mentioned in the introduction that one good example to prove this approach is wrong is $Yb:YVO_4$. We all know that $Nd:YVO_4$ is such an excellent laser crystal. One would expect that $Yb:YVO_4$ should also be good. This turns out to be totally wrong. There is extensive overlapping between the absorption and emission spectra making $Yb:YVO_4$ impossible to lase. I should also point out that the Y site in both YAG and YVO_4 are 8-fold coordinated dodecahedral site. This means that even with the same coordination site, we still can not predict the spectroscopic behavior of Yb ion.

We have investigated a number of laser hosts for possible Yb doping. We decided that we will be concentrated on congruent melting composition so that single crystals can be produced for investigation. We started with fluoride laser hosts since we have investigated many of them for other laser applications. The hosts include $LiYF_4$, KYF_4, BaY_2F_8. Unfortunately, none of them shows any exciting spectroscopic results after doping with Yb to make them worthwhile to investigate. We also search for oxide laser host materials. Unfortunately, there are only a few Y content congruent melting oxide compounds such as Y_2SiO_5 and $YAlO_3$. When doped with Yb, both of them show

reasonable spectroscopic properties but they are not as good as Yb:YAG. Thus there is no point to continue the investigation of these compounds.

In next section, we will discuss our effort to investigate non-linear optical crystals for frequency conversions. One crystal that we have investigated extensively is YCOB. This is one of very few known congruent melting non-linear optical crystals. Also since it has an Y site so that it can be doped with both Nd and Yb or any other rare earth ions. This makes them extremely attractive as a self-frequency doubling laser host. We have successfully doped the crystal with both Nd and Yb ions with high concentrations (up to 10 at% for Nd and 40 at% for Yb. Lasing can easily be achieved for both Nd and Yb doped crystals. We also achieve self-frequency doubling in both cases. We will discuss that in detail in the non-linear crystal section. Yb doped YCOB by its own virtue is a very good laser crystal.

In this investigation, we have looked into many possible Yb laser hosts. In addition to the spectroscopic properties, the thermal mechanical properties is also important since the diode pumped laser is tightly focused to the crystal so that there will be significant heat generation right at the lasing area. So far Yb:YAG laser is still the one which can take the highest power from the laser diode.

Growth of Large Nd:YAG Slabs:

In previous section, we have discussed in great detail of our research effort under this contract to search for laser hosts which can deliver more power than Nd:YAG. It turns out that Yb:YAG will the only one that can deliver more power than Nd:YAG. In both cases, heat removal is still a key factor to ensure high power delivery. High thermal conductivity is highly desired property. However, heat removal can be facilitated by proper geometry. What we need is to keep at least on of the dimension of the lasing medium small. Heat removal of glass fiber laser is very good because two of the dimensions are very small. But small aperture also limits the maximum fluency of power. A compromise will be the slab laser geometry so that one of the crystal dimensions is small. It makes the heat removal very effectively. Nd:YAG slab laser has been used successfully to deliver kilowatts of power with near diffraction limited beam profile. There is a need to produce real large Nd:YAG slabs for even higher power generation.

The standard method to produce Nd:YAG crystal is by pulling directly from the melt. Because of the (211) facet development, the crystal always has a core regardless whether it is grown along (001) or (111) direction. As a result the core region of YAG crystal is not usable. At the time when we start to look for alternative way to produce larger size slabs, typical Nd:YAG is only 3" in diameter. It is very difficult to produce slabs greater than 30 mm in width because of the core.

In mid 90's, I was aware about the work of Professor Badasaroff of the Institute of Crystallography, Russian Academy of Science. He has designed a high temperature

horizontal Bridgman furnace to grow sapphire single crystals. I went over to Russia to see the equipment. Based on their concept, we have redesigned and constructed a novel crystal growth furnace for the purpose to produce large Nd:YAG slabs. The principle is quite simple. It is based on horizontal zone melt traveling process. The difficult part is to deal with very high temperatures. There are only very limited methods that can heat a system to such high temperatures. There are also issues regarding to the insulation materials as well as the crucible materials. All of these are intricately related to each other. One can not consider just a single item without worry about the implication to others parts.

After considerable thinking, we decide to build a three zone horizontal induction heating furnace. Initially, we used three RF generators to power the furnace. We found that there is serious cross talk through RF coupling of the induction coils so that the signal from one generator will feed back to the other and blow the IGBTs. We made the change by replace three generators into a single one. We used a distributed coil design to deliver different power at each of the three zone furnace. This eliminated the feed back signal problem. After the power supply, the next issue is melt container and how to couple the power to the container. Since the YAG melt sticks well to all the metal containers, so that the metal container can only be used for one growth run. This rules out the use of Iridium container since it is just too expensive. We finally selected the molybdenum container to hold the melt. The reason is that molybdenum metal is not so expensive. It is also the metal of choice for the crystal growth effort in Russia. We were eventually able to find a vendor who can make the container for us. To increase

the power coupling, the moly-container is sitting on top of a tungsten metal plate which is the primary power coupler from the RF heating coil.

Our second task to get the system running is to make proper insulation during growth. This is because the furnace is in horizontal position. There is a lot heat generated during growth which moves upward through the induction coil. Proper insulation is needed. This turns out to be the major problem for the furnace. We need materials that are not conductive but refractory. They need to take the temperature up to 2000 but can also take the thermal shock so that it will not break during cooling. The process to design the thermal insulation took several months. We invited two major refractory material manufacturing companies to make the design for us. We have frequent discussions on the insulation design. Unfortunately, after all these efforts, neither one can give us a satisfactory design and they both back off in the last minutes. We finally had to make our own design. The insulation is made of both BN ceramic blocks and Zirconia blocks. The BN is used to take the thermal shock while the zirconia fives the true thermal insulation. Since all the parts are ceramic in nature, it is quite complicated to put them together. It is not the best design, but serve the purpose.

Finally, we need to design the power control system. We need feed back loop to control the power. In the beginning, we decided to use W-Rh high temperature thermal couples. The problem is that the thermal couple wire is very fragile after one heat-up cycle and very easy to break. We also have difficulty to position the thermal couple, since both the furnace is moving (or traveling) through the three heating zones, and the

location of melt/crystal interface is also moving. We have finally contact a company who are making high temperature optical thermometer using sapphire single crystal fiber as the light guide inside the furnace. We are able to measure the melt temperature more precisely with this optical thermometer. We also use its signal as the feedback to our power control system. It is not ideal, but this is the only viable solution that we can find. One unexpected draw back is that it takes a very long lead time (months) to replace the sapphire fiber. The tip of the sapphire fiber is exposed inside the furnace. The main problem is that there is material evaporation during the growth process. The evaporates will precipitate and coat the tip of the sapphire fiber making the sensor drifting with time.

After completing the construction of the furnace, we have conducted a number of experiments starting with low melting materials. We have no difficult to melt and freeze them into crystal plate. Unfortunately, the crystal plate is not single due to the lack of seed. We put the seed at one end of the crucible before growth. The main problem is that the linear temperature gradient is just too small. In order to melt the charges, the seed is always melted at the same time. By the time we supercool the charge, there are always more than one grain to form and thus it produces a polycrystalline plate. We have also tried a number of times to grow the Nd:YAG using the same equipment. Because of premixed powder has too much volume, we retreat to use crushed pre-grown Nd:YAG chunks as charge. Melting of this is slightly more difficult since the heat coupling is not as effective until after melting. In this case, we have the same problem regarding to the seed. We have made Nd:YAG crystal plates, but the quality is not so great.

The concept to use horizontal Bridgman zone melting is a neat way to produce large size slabs or bars of crystal with high perfection. It has been used successfully to produce low dislocation GaAs single crystal boules. The same technique is also used to grow oxide crystals. The best example is the growth BGO crystal as scintillator. At present time a few tons of BGO is produced annually using this technique. However, there is a major difference between GaAs and BGO vs Nd:YAG. The difference is the temperature. Crystals with melting temperature below 1500°C is extremely easy to handle since we have all the heating elements, insulations and containers to use. To push this to 2,000°C is a totally different game. All of a sudden, none of the known materials nor technology will work. So after seen the difficulty that Professor Badasaroff had for his tungsten resistance heating furnace design, we thought that we have a better solution to use RF induction heating. The result is quite comparable. Our heating is much easier than his system but our problem is to increase the longitudinal temperature gradient so that we can prevent the seed from melting.

Search for New Nonlinear Optical Materials:

Despite the extensive research on solid state laser materials, there are only very few of them that are good enough to make to the commercial market. Among them, Nd:YAG is still the only one that dominates the market. Because of this, the available wavelengths of coherent light sources directly from active lasers are quite limited.

Fortunately, it is possible to convert the lasing wavelength to others through nonlinear process such as SHG, OPO, SFM and DFM etc. However, one should know that the nonlinear conversion is not a very efficient process. It is highly critical to have good nonlinear crystals that can improve the efficiency. Again, similar to laser crystals, there are a fair number of known non-linear optical crystals but the usable one is only a few. This is the primary reason that there is always the interest to continue the search for new nonlinear optical crystals.

The search for nonlinear optical crystals is also a non-trivial process. However, in this case, the rules are much clearer. The three basic requirements are:

(1) non-centrosymmetric,

(2) high birefrigence,

(3) high optical nonlinearity.

Even though the rules are quite simple and clear for each of the requirement, to be able to find materials that can satisfy all three requirements at the same time are very difficult. Among the three issues, high birefrigence turns our to be the most difficult one to meet. In addition to these three requirements, there are also the basic material requirements such as physically strong, no mica-like cleavage planes, non-hygroscopic, etc. The last and final requirement is that it is capable to grow large size crystals at reasonable cost.

Many early day findings of nonlinear crystals such as KDP which is still in use today. Because of the water solubility, special enclosure is needed to house the crystal. For many practical usages, it is preferred that the crystal is not hygroscopic. Over the past two decades, a few newly discovered non-linear crystals have made to the market, namely, KTP, BBO and LBO. They have the advantage of having sufficient birefrigence so that they can frequency double, triple and quadruple the Nd:YAG 1.06 μm laser efficiently into the visible and UV light region. The optical damage thresholds of these crystals are also adequate for most practical applications. The only disadvantage is that none of these crystals melt congruently so that they all have to grow from flux. The growth rate is slow and the crystal size is also limited. This limits the size of the crystal aperture that can be used for really high power applications. This situation has sustained for a number of years without a real solution.

In mid-90's, there were reports from France about a new nonlinear borate crystal which is congruent melting and non-hygroscopic. This creates a lot excitement. Moreover, since the crystal has a substitution site for rare-earth ions, this makes the self-frequency doubling scheme workable. The crystal is GdCOB ($GdCa_4(BO_3)_3O$). It is one member of the rare-earth calcium oxyborate family compounds which was first reported in 1991. We have investigated extensively this crystal system in our laboratory under this contract. The composition that we have spent most of the time on is YCOB ($YCa_4(BO_3)_3O$). Over the course of research, we have produced two Ph.D. theses that are based on this investigation. More than one dozen of papers have been published based on this work.

Both GdCOB and YCOB are quite unique such that they are the true congruent melting compounds without phase transition from melting temperature down to room temperature. Most of the known congruent melting borates are centrosymmetric. This is a truly exception. Both high quality and very large size crystals of GdCOB and YCOB have produced at our laboratory. Non-linear properties were checked. It is possible to achieve Type I phase matching at 1.06 μm for both crystals. YCOB has slightly higher birefrigence and thus phase matchable for 3rd harmonic generation. Similar to BBO and LBO, the optical nonlinearity of both GdCOB and YCOB is derived from the same borate group and thus they all have quite comparable values. We have made effort to tune the optical properties of these crystals with composition. We found that we were only able to modify in a very small degree of either the optical nonlinearity or the birefrigence. It is not so flexible to find non-critical phase matching composition for a particular wavelength.

One nice feature of these crystals is the congruent melting. Now, it is possible to grow very large size crystal to provide large aperture for high power laser application. In fact, they are the only nonlinear borate crystals capable to do so. In addition to be nice nonlinear crystals, they also can be used as laser hosts since they have a natural rare earth site so that the substitution with active ions is not a problem. I have mentioned in the previous section that we were able to lase both Nd and Yb doped YCOB and GdCOB crystals.

The most interesting part of this research is that we have one of the extremely rare chance to have a crystal that has the capability to combine the doping of active ions and optical nonlinearity in one for self-frequency doubling. There is only one crystal before this one that has the same property. It is NYAB ($Nd:YAl_3(BO_3)_4$). There was great interest to develop NYAB as self-frequency doubling crystal for commercial use despite the great difficulty to grow it in flux. Now we have a crystal which can do essentially the same and can be grown easily in large, high quality crystals. Indeed, once we have developed the growth process, we immediately doped it with almost all the rare earth elements for spectroscopic study. The two special ones are Nd and Yb doped crystals.

In the case of Nd doping YCOB, we have produced both green (530 nm) and red (660 nm) color by self-frequency doubling. We were the first place that have successfully achieve the lasing in the red. Self-frequency doubling in the blue region is not successful due to the lower emission cross-section of the 944 nm peak. We also attempted the self-frequency doubling of Yb doped YCOB. We are able to demonstrate the green emission. But it is extremely unstable due to the broad ban emission of the Yb laser. Self-frequency doubling causes the depletion (or lower the gain) of the specific lasing level and lasing is shift to another wavelength which has higher gain. When that one is depleted due to self-frequency doubling, the lasing hops to another wavelength. As a result, the green conversion spectra are highly spiky and unstable. We concluded that self-frequency doubling works with Nd doping which has fixed specific energy level and will not work on Yb system due to the broad continuous emission.

We have spent a lot effort trying to develop Nd:YCOB and/or Nd:GdCOB into a commercial product. But it was not as successful as we would like to see. The reason at the beginning is not so clear. In the end, it is the cost versus performance issue. Even though we have a crystal that combines both lasing and nonlinear conversion into one and thus simplifies the laser system and reduces the crystal cost, however, we find two drawbacks that prove to be detrimental for the commercialization of these crystals.

(1) When we have one crystal for both lasing and nonlinear conversion, we need special coating on both side of the crystal surface to achieve it. This is more expensive but achievable. Our challenge is how to cut the crystal right on the orientation since the angle of acceptance is quite small for Type I critical phase matching so the tolerance of cutting accuracy is also very small. If by any chance that the angle is off, there is no recourse to correct it, since there is no part within the cavity that can be adjusted. In the traditional design, we can adjust both the laser crystal and the nonlinear crystal to maximize the output. So far we have great difficulty to cut and polish them accurate enough for mass production.

(2) Even though the crystal is both a laser and a nonlinear frequency converter, the performance of lasing can not be compared with Nd:YVO_4, nor the performance of nonlinear conversion be compared with that of KTP. As a result the combination of Nd:YVO_4 + KTP can easily outperform Nd:YCOB or Nd:GdCOB with much lasing threshold and higher slope efficiency. Now

it is a matter of laser diode size and the battery lifetime. So for the green pointer application, Nd:YCOB will need a 500 mW laser diode while the Nd:YVO_4 + KTP combination only needs a 250 mW laser diode and a new pack of battery will last twice as much time. Moreover, the extra cost of the high power laser diode for Nd:YCOB almost push for the extra cost of having Nd:YVO_4 and KTP two crystals.

In any respect, this is a good learning lesson. There are more than one issues that need to consider when to look for a success entry in the commercial market. Right now both YCOB and GdCOB have its value as nonlinear optical crystal because of the large aperture and also more competitive price as compared to BBO and LBO. It is unlikely that they will be successful as a self-frequency doubling crystals.

Summary and Conclusion:

Under this contract we have performed three different tasks as stated in this final report. I have made detailed description of each task. Research into the total unknown is both challenging and exciting. We have made our effort to do our best given the total uncertainty of any success. To look back, we have achieved a lot. We may not find the holy grill. But we do know what is the limitation. If the limitation is due technical difficulty, there is a chance for the breakthrough. If the limitation is due to physical or material reasons, then there is no chance to see the breakthrough since we can not violet

the fundamental rules of physics and chemistry. It can prevent future fortuitous research which may not produce anything at all.

For the new high average power laser materials, it is highly unlikely that we will find materials capable to be doped with Nd and having better thermal mechanical strength over YAG. Nd doped lutetia (Lu_2O_3) might be our only chance. Yb:YAG is clearly a winner over Nd:YAG. But it will restricted to diode pumping only and the system may have to be chilled in order to increase the efficiency. Yb:Lu_2O_3 has its chance but only if the spectroscopic result looks good and the crystal growth problem can be resolved.

For the YAG slab growth project, our limitation is the heating method and the insulation materials. This is more of a technical problem. Still to be able to find materials that can take 2000°C temperature and not cracking when go through the thermal cycle is a true challenge. Horizontal Bridgman zone melting crystal growth system works well as low temperatures. It requires more research to overcome the temperature problem.

For the new nonlinear optical crystals, YCOB and GdCOB offer the unique property of congruent melting. This makes the growth of large single crystal possible at reasonable rate. This will be the only non-water soluble nonlinear crystal that can offer large aperture for high power laser applications. Because of the rare earth site, the crystal can also be used as laser host. While the performance of Nd doped YCOB or

GdCOB is quite average. the Yb doped ones have much better performance. We have achieved self frequency doubling in the green and red with Nd doped YCOB. It is an attractive but not quite practical for commercial applications. We also observed self frequency doubling signal in Yb doped YCOB. But this is a totally wrong application. We believe that both YCOB and GdCOB will have their best chance to be used just as a good large aperture nonlinear frequency converters.

Attachments:

I am attached here three Ph.D. thesis which were worked under this contract to investigate the material:

(1) Investigation of Self-Frequency Doubling Crystals, $YCa_4O(BO_3)_3$ (YCOB) doped with Neodymium and Ytterbium, by Qing Ye, 1999

(2) Power Scaling of Diode-pumped Nd^{3+} and Yb^{3+} doped $YCa_4O(BO_3)_3$ (YCOB), A New Self-frequency Doubling Laser, by Dennis Hammons, 2000

(3) Yb^{3+}:$Sr_3(VO_4)_3F$ Crescimento, Caracterizacao Espectroscopica e Desenvolvimento do Laser, by Andrea Nora Pino Bustamante, 1999